

**Chemistry Quiz
Chemical Kinetics
Instructor's Version B**

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Answer Sheet

1.	A
2.	B
3.	B
4.	D
5.	C
6.	C
7.	C
8.	E
9.	A
10.	D

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Free-Response Questions

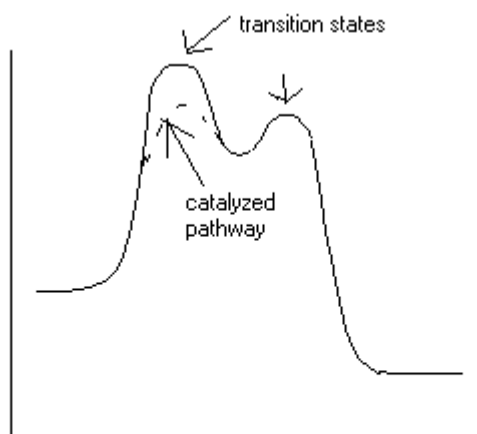
Time Limit: You have 30 minutes to complete this section.

Scoring: 60 points total; Question 1 is worth 40 points and Question 2 is worth 20 points; points for each section are indicated within the questions.

Calculator Use: You may use a calculator on both questions.

1. A reaction occurs which is exothermic and has a 2-step mechanism.

A. Draw a potential energy vs. reaction coordinate graph of this reaction. (Your answers to b and c are graded independently of a correct or incorrect graph in part A)



A: Show solid line only (uncatalyzed pathway)

B: Show transition states

C: Show dashed line as well (catalyzed pathway)

B. Indicate on the graph where the transition state(s) is (are)?

See above graph

C. Show how the graph would change with the addition of a catalyst, which would act in the first step only.

See above graph

D. How does increasing the temperature increase the rate? Explain on a molecular level.

Increasing the temperature means increasing the number of collisions and therefore the likelihood of a reaction, therefore increasing the rate. The rate constant is temperature dependent (they may add the equation $k = Ae^{-E_a/RT}$), and as temperature increases, the rate increases. (This does NOT need to include arguments for equilibrium conditions- in any case the rate forward and reverse both increase with an increase in temperature, but for equilibria the final shift depends on exo or endo reactions, and does not apply here).

E. Does every collision result in a reaction? Explain.

Not every collision results in a reaction. First, the collision must have enough kinetic energy to overcome the activation energy. Second, the reacting particles must have the right orientation.

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2. For the reaction: $A + B + C \rightarrow D$ the following data were taken:

	[A] (M)	[B] (M)	[C] (M)	Rate (M/s) of D
Experiment 1	1.5	1.5	1.5	2.40×10^{-2}
Experiment 2	1.5	2.5	1.5	2.40×10^{-2}
Experiment 3	3.0	1.5	1.5	4.80×10^{-2}
Experiment 4	4.5	1.5	3.0	1.44×10^{-1}

A. Write an expression for the rate law. Explain.

From experiments 1 and 2, while the concentration of B increases (others constant), there is no change in the rate. Therefore, the reaction is zero order in [B].

From experiments 1 and 3 the [A] doubles (others constant), while the rate doubles. Therefore, the reaction is first order in A.

From experiments 1 and 4, the [A] triples (B is constant), while the [C] doubles. The rate increases by a factor of 6. The tripling of [A] accounts for a tripling of the rate. The fact that it is doubled again beyond that, while [C] is double, indicates a first order in C.

NOTE: the more eloquent way of solving this using ratios of experiments might be used and is perfectly, if not more, acceptable.

B. Calculate the value for k.

The value for $k = \text{rate} / \text{concentrations}$ for any of the experiments: $k = 1.1 \times 10^{-2} \text{ L/mol s}$

C. Which of the following mechanisms is acceptable. Show why in terms of the rate law and the overall stoichiometry.

Mechanism I:	Step 1	$A + B \rightarrow X$	(slow)
	Step 2	$X + C \rightarrow D$	(fast)
Mechanism II:	Step 1	$A + B \rightleftharpoons X$	(fast equilibrium)
	Step 2	$X + C \rightarrow D$	(slow)
Mechanism III:	Step 1	$A \rightleftharpoons X$	(fast equilibrium)
	Step 2	$X + C \rightarrow Y$	(slow)
	Step 3	$Y + B \rightarrow D$	(fast)

Mechanism III is acceptable:

Step 1: (forward) $\text{rate}_f = k_f[A] = \text{rate}_r = k_r[X]$

Setting the rates equal for the first step, we get: $[X] = k_f/k_r[A]$

Step 2: $\text{rate}_2 = k_2[X][C]$

Substituting for $[X]$ we get: $\text{rate}_2 = k_2k_f/k_r[A][C]$

Combining rate constants into one, this will match the overall rate law, confirming that this is an acceptable mechanism in terms of the slow and preceding steps.

The overall stoichiometry also matches the overall equation, since X and Y cancel out, leaving just $A + B + C \rightarrow D$.